Electronic Supplementary Material (ESI) for RSC Advances.

Total Synthesis of Cruciferane *via* Epoxidation/Tandem Cyclization Sequence

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Experimental Section:

General Information:

^{1}H and ^{13}C-NMR spectra were recorded at 400 and 100 MHz, respectively, or at 500 and 125 MHz, respectively. Chemical shifts were calculated in ppm downfield from TMS (δ = 0) for ^{1}H NMR, and relative to the central $CDCl_3$ resonance (δ = 77.0) and DMSO-d_6 (δ = 39.51) for ^{13}C NMR. Data presented in the experimental section are as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=doublet doublet), coupling constant in Hertz (Hz). X-ray diffraction measurements were carried out at 298 K on an automated diffractometer using graphite-monochromated Mo-Ka (l = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on an instrument equipped with a graphite monochromator and a Mo-Ka fine-focus sealed tube (l = 0.71073 Å). TOF and quadrupole mass analyzer types are used for the HRMS measurements. Mass spectral data was obtained from HRMS (ESI). IR spectra were recorded on a FT-IR spectrometer using KBr pellets. Melting points were measured in open capillary tubes and are uncorrected. All the obtained products were purified by column chromatography using silica gel (100-200 mesh). All reaction solvents used were dried from GR grade solvents. All other commercial reagents were used as received.

Preparation of 2-(2-1*H*-indol-3-yl-acetylamino)-benzoic acid methyl ester (2):

To a suspension of **1a** (200 mg, 1.0 mmol) in 10 mL of dry dichloromethane at 0 °C were added oxalyl chloride (0.48 mL, 5.7 mmol, 5.0 equiv) dropwise and DMF (3 drops) successively. The mixture was stirred at 0 °C for 3 h and concentrated under vacuum to give 287 mg of crude 1*H*-indole-3-acetyl chloride, which was utilized for the synthesis of **2** without further purification. Then, to the solution of methyl anthranilate **1b** prepared via literature procedure[17] (224 mg, 1.3 mmol) and Et_3N (0.80 mL, 5.0 mmol) in 10 mL of DCM at 0 °C was added a solution of crude **1a** (287 mg from (200mg of **1a**)) in 4 mL of DCM. The reaction mixture was stirred at room temperature for 5 h and concentrated under vacuum. To the residue was added 15 mL of saturated water. The mixture was extracted with EtOAc (30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. Flash chromatography of the residue on silica gel (7:3 hexanes/ EtOAc) gave 272 mg of compound **2** as light brownish solid; yield = 78 %; m.p. (HPLC grade Hexane/ ethyl acetate)= 136-140 ^oC ; IR (KBr) 3205, 2947, 1698, 1654, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.96 (1H, s), 8.74 (1H, d, J = 8.0 Hz), 8.33 (1H, s, br), 7.92 (1H, dd, J = 1.2 Hz, J = 8.0 Hz), 7.66 (1H, d, J = 8.0 Hz), 7.51 (1H, t, J = 8.0 Hz), 7.39 (1H, d, J = 8.0 Hz), 7.29 (1H, s), 7.21 (1H, t, J = 7.2 Hz), 7.13 (1H, t, J = 7.2 Hz), 7.04 (1H, t, J = 8.0 Hz), 3.94 (2H, s), 3.70 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ aromatic: 170.8, 168.1, 141.1, 136.5, 134.4, 130.7, 127.4, 123.9, 122.5, 122.4, 120.5, 119.9, 118.9, 115.5, 111.2, 108.7, aliphatic: 52.1, 35.6 ; HRMS (ESI-MS) cald. for $C_{18}H_{16}N_2O_3$ (M+Na) 331.1059; found 331.1061.

Preparation of 2-(3a-hydroxy-2-oxo-3,3a,8,8a-tetrahydro-2*H*-pyrrolo[2,3-*b*]indol-1-yl)-benzoic acid methyl ester (4):

To a solution of compound **2** (50 mg, 0.16 mmol) in anhydrous acetone (4 mL) was added dropwise a solution of DMDO (prepared by Taber's method)[18] in acetone (0.021 M, 7.7 ml, 0.64 mmol) at –78 °C. Reaction mixture was stirred at the same temperature for 6 h, then temperature was increased to rt and stirred for additional 2 h at rt. Then to the reaction mixture 20 ml water was added and resulting mixture was extracted from EtOAc (30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexanes: EtOAc = 2:8) to give compound **4** as white solid; yield = (44 mg, 85 %); m.p. (HPLC grade Hexane/ ethyl acetate) = 72- 76 ^oC ; IR (Neat) 3313, 2921, 1710, 1676, 1604, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO- d_6) δ 7.81 (1H, d, J = 8.0 Hz), 7.66 (1H, t, J = 8.0 Hz), 7.45 (1H, t, J = 7.2 Hz), 7.32 (2H, t, J = 7.2 Hz), 7.11 (1H, t, J = 7.6 Hz), 6.73 (1H, t, J = 7.2 Hz), 6.64 (1H, s), 6.58 (1H, d, J = 7.6 Hz), 6.04 (1H, s), 5.40 (1H, d, J = 4.0 Hz), 3.38 (3H, s), 2.96 (1H, d, J = 16.8 Hz), 2.90 (1H, d, J = 17.6 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ aromatic: 171.9, 166.1, 148.2, 136.1, 132.2, 131.8, 131.4, 130.9, 130.0, 129.3, 128.5, 124.3, 120.8, 111.4, aliphatic: 85.4, 81.9, 52.3, 43.6 ; HRMS (ESI-MS) cald. for $C_{18}H_{16}N_2O_4$ (M+Na) 347.1008; found 347.1008.

Preparation of Cruciferane (5):

To a solution of compound **4** (30 mg, 0.09 mmol) in MeOH (3 mL) was added a solution of freshly prepared CH_3ONa (19 mg, 0.36 mmol) in CH_3OH (3 mL) at -10 °C. The reaction mixture was stirred for 5 h at the same temperature; afterwards mixture was kept at rt stirring for additional 1 hr. After completion of reaction (checked by TLC), 10 ml of water was added to the

reaction and the residue was extracted with EtOAc (20 mL). The combined organic layers was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes:EtOAc = 7:3) to give compound **5** as white solid. This compound **5** was obtained as white solid; yield = (25 mg, 91 %) m.p. (HPLC grade Hexane/ ethyl acetate) = 208- 210 ^{o}C ; IR (KBr) 3328, 2920, 1721, 1644, 1602, 824 cm^{-1}; ^{1}H NMR (400 MHz, DMSO- d_6) δ 8.02 (1H, d, J = 8.0 Hz), 7.91 (1H, d, J = 8.0 Hz), 7.75- 7.70 (2H, m), 7.53 (1H, d, J = 7.04 Hz), 7.47- 7.38 (2H, m), 7.21 (1H, t, J = 7.2 Hz), 6.70 (1H, s), 5.79 (1H, s), 3.15 (1H, d, J = 18.4 Hz), 3.04 (1H, d, J = 18.4 Hz); ^{13}C NMR (100 MHz, DMSO- d_6) δ aromatic: 170.3, 158.5, 140.2, 136.3, 135.3, 133.5, 129.8, 128.3, 126.0, 124.8, 124.5, 123.3, 121.9, 114.7 aliphatic: 82.4, 77.4, 45.7 ; HRMS (ESI-MS) cald. for $C_{17}H_{12}N_2O_3$ (M+H) 293.0926; found 293.0924.

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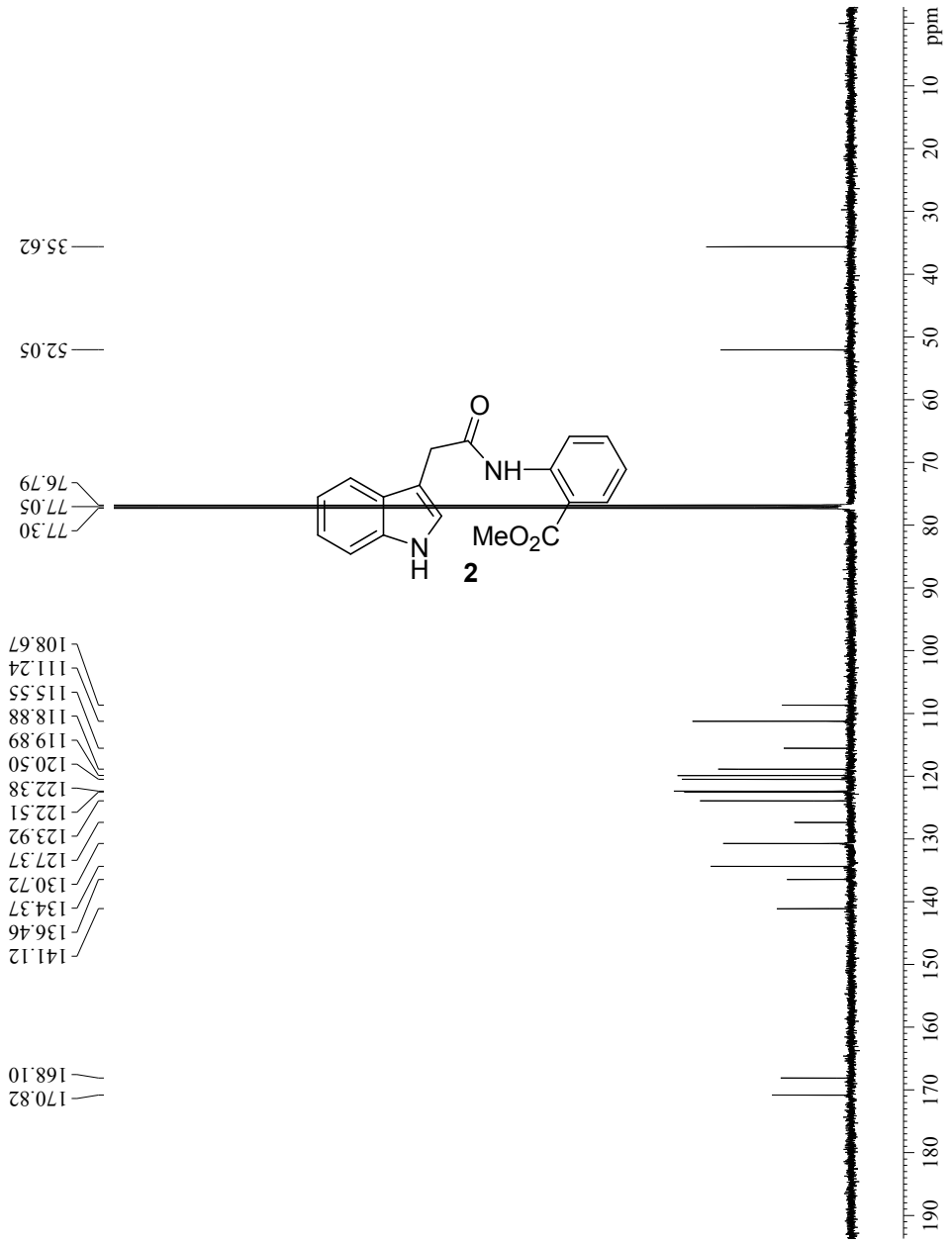
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Analysis Info

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Comment			

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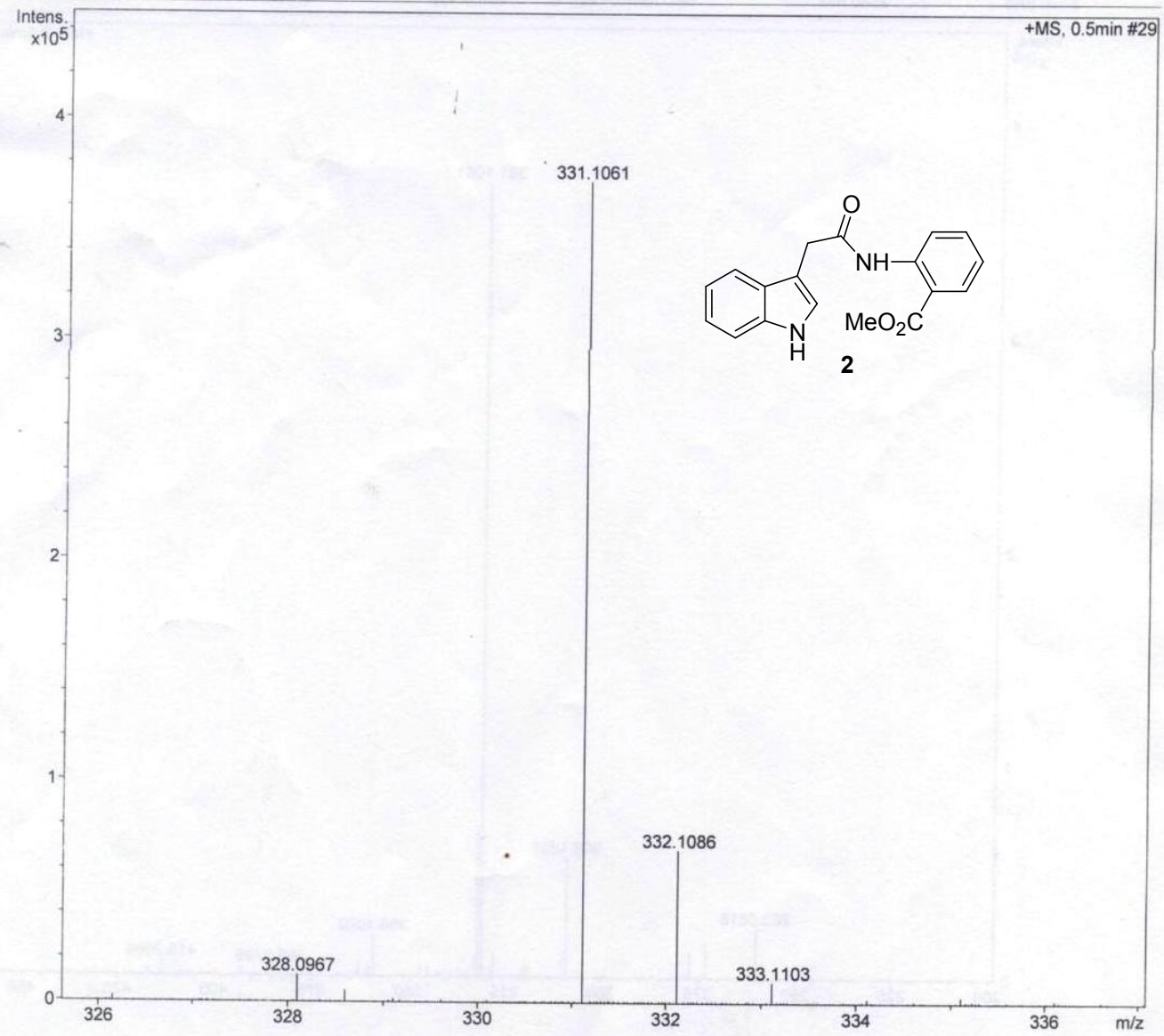

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Analysis Info

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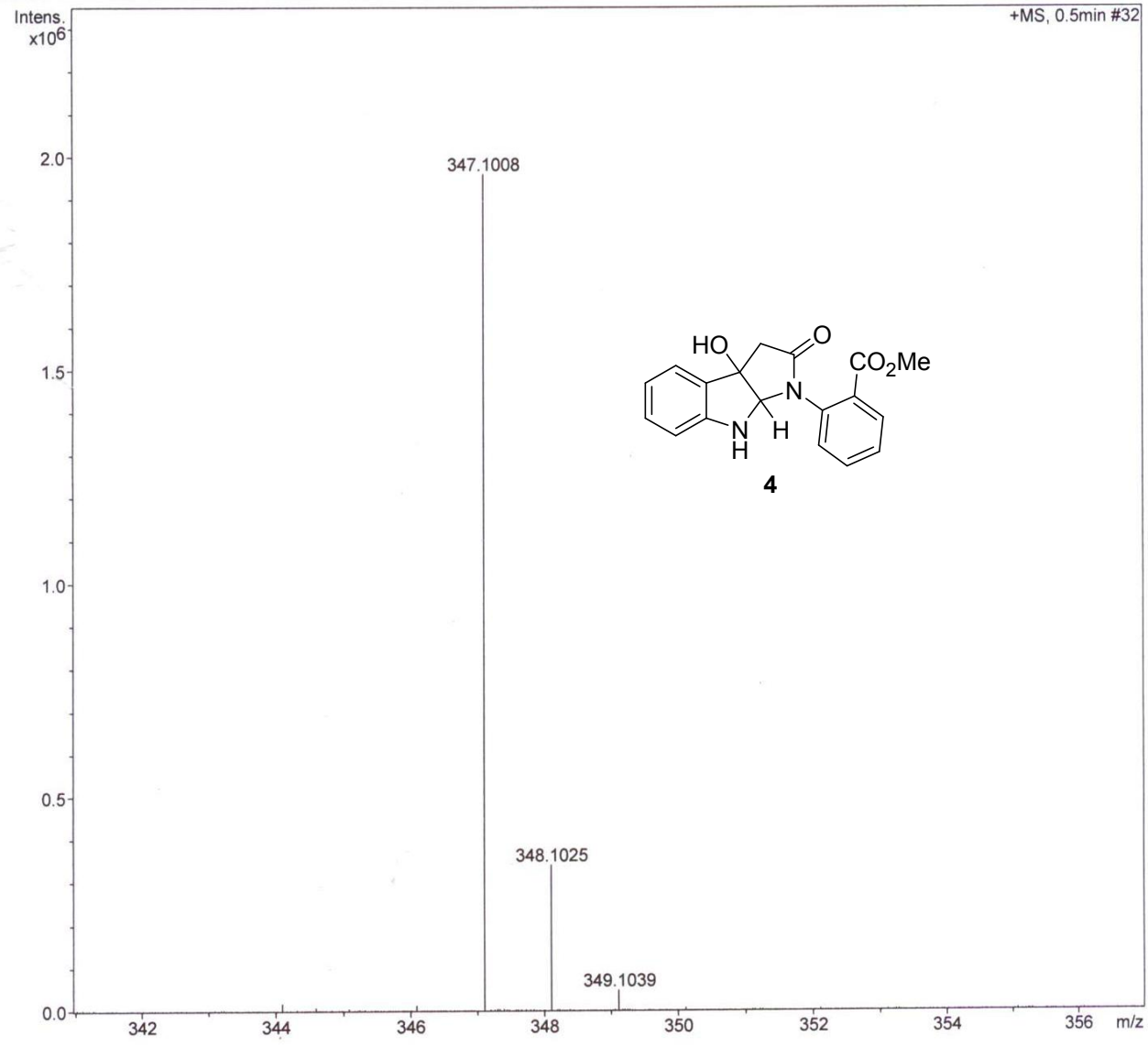

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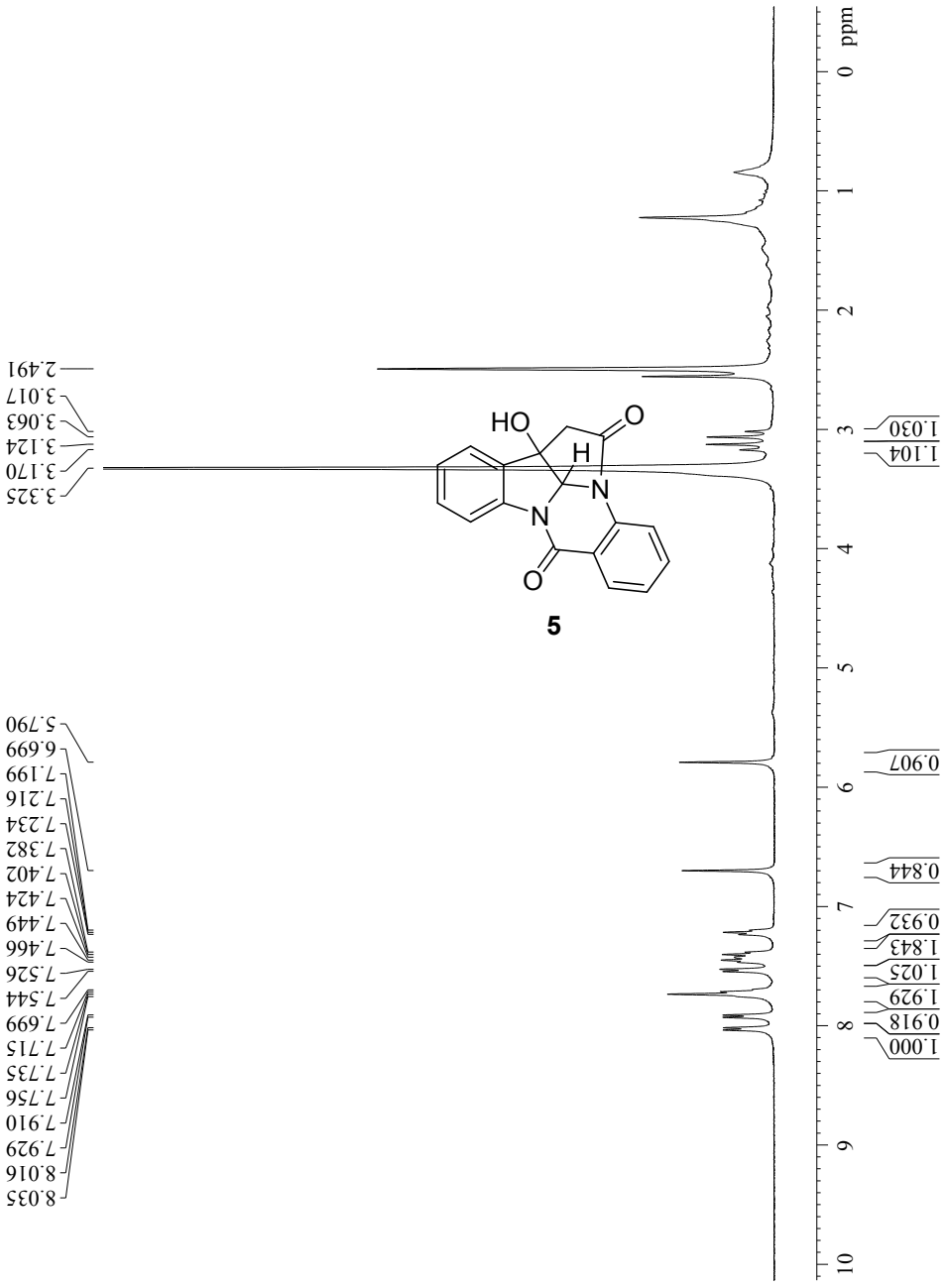
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Analysis Info

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